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Exploring Athermal Initiation Mechanisms of Azides

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Abstract. We performed quantum chemical calculations to explore the possibility of athermal initiation mechanisms in azide-containing explosives. Our calculations showed that bending (i.e. shear) of the N-N-N bond in N_3^- *decreases* the HOMO-LUMO energy gap from an initial 4 eV to 1.9 eV at a bending angle $\gamma=120º$. This indicates that the material could become semi-conductor, but *not* metallic. Molecular dynamics simulations on ionic NaN_3 at various temperatures also showed that the N-N-N bending motion is in the range of 150°-180° for T=600-3000 °K. No bending to $\gamma=120º$ is observed. At higher T, simulations showed that NaN_3 decomposes to Na and N_2. We also explored the athermal mechanism due to electronic excitation followed by *non-radiative* decay. We calculated the energy curves of the ground and the excited state of N_3^-, and the ground state of N_3 as a function of the N-N-N bending angle. We found significant interstate crossing (degeneracy) between the two lowest states of N_3^- occurring in the bending region of 100º-125º. If energy to cause electronic excitation is available via shock compression, then intersystem crossings lead to energy de-excitation to the ground state. This energy channeling is *non-radiative* (kinetic) in nature, generating vibrationally hot ground state molecules that speed up towards decomposition. Finally, our quantum calculations showed the possible existence of $N_3(N_3)^-$ complex and N_6, both of which are thermodynamically stable relative to the azide fragments (N_3). It is proposed that this complex, or an infinite, periodic N_3–N_3^- chain might be formed upon moderate heating (T~600 °K), or via moderate pressure on sodium azide due to shock, representing a prelude to the exothermic decomposition into final metallic Na and N_2 products.

Introduction

Lead azide $[Pb(N_3)_2]$ is a powerful explosive used as an initiator in blasting caps and detonators. It is extremely sensitive to spark, impact, and friction. Sodium azide (NaN_3), however, is an excellent propellant, but is not a detonable explosive, while lithium azide (LiN_3) is.[1] Despite similar, simple elemental composition of azide anion (N_3^-) and metal cations, and correspondingly similar decomposition products, these materials exhibit dramatic differences in sensitivity and performance towards external stimuli. While the electronic structure is expected to be intimately related to their initiation and decomposition processes, there is no systematic or mechanistic study to date that offers a unified and a consistent explanation of the varied responses of metal azides.

Several athermal mechanisms have been proposed relating to the initial effect of mechanical energy transfer from a shock front to explosive

molecules. Gilman has long noted that detonation fronts in lead azide, for example, are too fast to be thermally activated. [2] Instead, he proposed that detonation fronts are athermally activated by causing local metallization via shear strains whose effects are to raise the energies of the bonding electrons and lowering the energies of the anti bonding electrons, thus closing the HOMO-LUMO gap and eliminating the activation energy for decomposition. [3] Ab initio calculations showed that in the case of TATB, out-of-plane bending of the nitro group by 55º causes its HOMO-LUMO gap to vanish. [4] Others have investigated the causes and effects of electronic excitation in nitro-containing explosive molecules and solids. [5,6] It was noted that if electronic excitation is involved in initiation, intersystem crossings; region of degeneracy between the lowest excited state and the ground electronic states of the molecule, would lead to non-radiative energy re-channeling that produce vibrationally hot ground state molecules. Interestingly, these regions of intersection exist via out-of-plane bending motion of the nitro group in the respective explosive molecule.

In this work, we perform first principles, density functional (DFT) and quantum chemical, second-order Møller-Plesset (MP2), Quadratic Configuration Interaction with Single and Double substitutions (QCISD) calculations, and density functional molecular dynamics simulations to investigate three athermal initiation mechanisms of metal azides. We calculated the HOMO-LUMO energy gap as a function of the N-N-N bending (shear) angle in N_3^-. We performed molecular dynamics (MD) simulations at various temperatures and monitored the propensity of the N-N-N bending motion for temperatures in the range, T=600-3000 °K. We also determined the fully optimized electronic energy curves of the ground electronic singlet and the lowest triplet states of N_3^-, and the ground electronic doublet state of $N_3^.$ (radical) as a function of the bending angle. Finally, our quantum calculations showed the possible existence of N_3 $(N_3)^-$ complex and several N_6 structures, all of which are thermodynamically stable relative to their azide fragments (N_3).

Results

First, we considered the electronic structure of solid lead azide, $Pb(N_3)_2$, and sodium azide, NaN_3. Density functional calculations determined that sodium azide is an insulator with a band gap of about 4.7 eV (Figure 1), and is ionic in nature (i.e. $Na^+N_3^-$). Calculations also showed that lead azide can be considered as a semiconductor, with a band gap of about 2.5 eV, in good agreement with a recent study. [7]
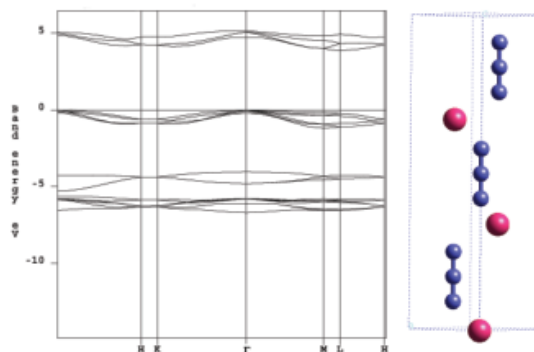

Fig. 1. DFT calculated band structure of NaN_3.

The molecular azide ion N_3^- has a linear equilibrium geometry (N-N-N bond angle γ=180º) in its ground electronic state (singlet state), with a N-N bond distance R=1.179Å as calculated at the DFTT/B3LYP level of theory using the augmented correlation consistent pVTZ basis set (R=1.181Å at the QCISD level with the same basis). The lowest triplet electronic state has a bent geometry as shown in Figure 2. DFT/B3LYP calculations locate this minimum with R_1=1.253Å, R_2=1.254Å, and γ=128.3º. As noted above, Gilman's proposed mechanism of shear induced metallization can be put to the test by determination of the electronic bonding/anti-bonding energy levels- the so-called energy difference of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), as a function of bending the N-N-N angle. Our calculations show that the HOMO-LUMO energy gap is monotonically decreased to 1.9 eV at γ=120º, from 4.7 eV at γ=180º, then rising again with further

decreased in γ. Figure 3 displays this behavior at the DFT level of calculations.
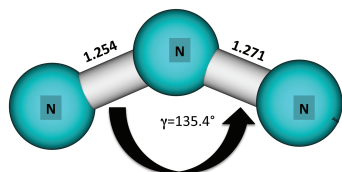

Fig. 2. QCISD equilibrium geometric structure of N_3^- in the excited triplet state.

The optimization procedure is carried out by fixing the angle at a certain value, while minimizing the energy of the ground state with respect to the two bond distances R_1 and R_2. We note that the decrease in the bending motion is associated with a monotonic increase in the symmetric stretch of equal bond distances, $R_1=R_2$ up to γ=90º. Further decrease in γ shows a marked departure towards dissociation of one nitrogen atom via R_2.
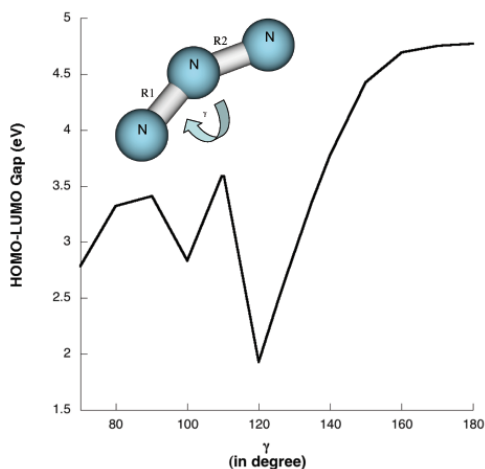

Fig. 3. DFT/B3LYP HOMO-LUMO energy gap as a function of the N-N-N bending angle in N_3^-.

The HOMO-LUMO gap behavior via shear bending as displayed in Fig. 3 indicates that for purely ionic NaN_3 the material could become semi-conductor, but *not* metallic. This perhaps explains the lack of initiation of this material via Gilman's criteria of metallization. We further performed DFT simulations at constant volume-temperature of NaN_3. These simulations showed that the N-N-N bending motion is in the range of 150°-180° for T=600-3000 °K. No bending to γ=120º is observed. At higher T, NaN_3 decomposed into Na and N_2. We note that lead and lithium azides exhibit greater covalent bonding character, and bending of the azide in these systems may result in a complete band closure (metallization). This, however, remains to be examined.

The second athermal mechanism (mentioned above) examines the energy re-distribution following an electronic excitation of the azide ion to the lowest accessible electronic state. Since electrons are much lighter than the nuclei, and thus move much faster, it is presumed that they could respond first to an external stimulus. To this end, we calculated the energy curves of the ground and the excited state of N_3^-, and the ground state of N_3 radical as a function of the N-N-N bending angle. Figure 4 displays the DFT/B3LYP results.
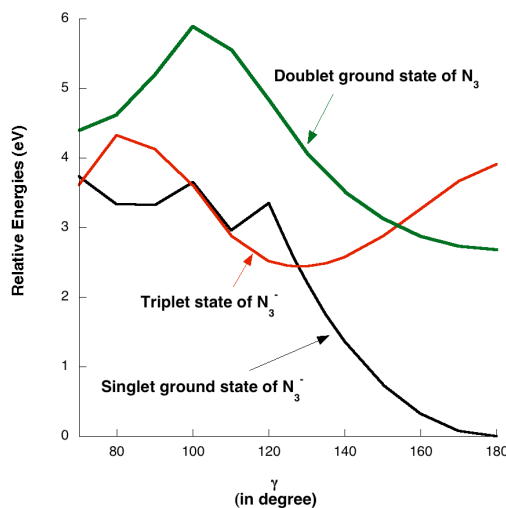

Fig. 4. DFT/B3LYP fully optimized energy curves of singlet and excited state of N_3^-, and the doublet ground state of N_3 radical as a function of N-N-N bending.

As shown in Fig. 4, there is a region of significant interstate crossing (degeneracy) between the two lowest states of N_3^- occurring in the bending region of 100º-125º. The energetic is such that the electronic excitation from the ground state to the triplet state in N_3^- requires an initial 4 eV. If this energy is available via shock compression, then intersystem crossings lead to energy de-excitation to the ground state. This energy channeling is expected to be fast (10 ~ 500 ps), and *non-radiative* (kinetic) in nature, generating vibrationally hot ground state molecules that speed up towards decomposition.

Finally, we consider the formation of "polynitrogen" as an intermediate step in the initiation process. While thermal decomposition mechanisms of heavy metal azides assume that the energy transformations of an explosion are established by the exothermic reaction: $2N_3 \rightarrow N_6 \rightarrow 3N_2 + Q \sim 10$ eV, we have investigated possible formation of ionic N_6. Our quantum calculations showed the possible existence of $N_3 (N_3)^-$ complex (Fig. 5). We find that this complex is thermodynamically stable with respect to dissociation into the corresponding azide fragments. The structure of this bound complex shows that the N_3–N_3^- bond is about 2.5 Å in length, slightly less than the distance separating two azide ions in crystal NaN_3 at ambient conditions. Unique IR and Raman spectroscopic signatures suggest the possibility of this complex being formed upon moderate heating of NaN_3 (T~600 °K). [8] It is also possible that infinite, periodic N_3–N_3^- chain is formed via charge transfer as a prelude to decomposition of NaN_3 into its final products. Computational work is currently underway to investigate this possibility, along with the concurrent development of associated charge transfer model upon feasibility.

Based on experimental evidence for silver azide, a process of chain mechanism has been favored over the thermal mechanism, and a model based on the role of electronic excitations facilitated by edge dislocations was subsequently proposed. [9,10] In this model, the formation of a molecular bond between the radical N_3 localized at a vacancy and the N_3^- ion is envisioned, similar to the hole self trapping process in alkali metal halides. [11] It may well be that the structure of the complex that we located and shown in Figure 5 can also be formed via their proposed mechanism in AgN_3.
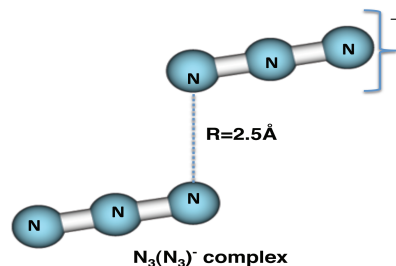

R=2.5Å

$N_3(N_3)^-$ complex

Fig. 5. DFT/B3LYP fully optimized structure of $N_3 (N_3)^-$ complex.

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